



UNITED STATES AIR FORCE RESEARCH LABORATORY

COMPUTATIONAL CHEMISTRY FOR THE HIGH POWER MICROWAVE INITIATIVE

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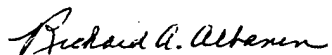
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FINAL REPORT

1.0 SECTION I: Introduction, Summary and Conclusions

1.1 Introduction and Background

Research groups within the Directed Energy Bioeffects Division, Human Effectiveness Directorate, Air Force Research Laboratory, Brooks Air Force Base, TX are jointly addressing the biomedical effects of exposure to electromagnetic radiation. One line of research is on mathematical and physical analysis of phenomena and data related to the biomedical effects of electromagnetic exposure. Another is on the development and application of experimental techniques for the determination of biomedical effects. In the past 10 years this Division has developed a chemical, diazolumelanin (DALM). The luminescence of DALM increases when irradiated by electromagnetic fields. The luminescence appears to be directly proportional to the temperature of the medium within which the molecular species resides, but the luminescent response is also a function of other medium properties such as salt content. DALM may be a prototype molecule in the sense that it appears to be highly sensitive to the temperature of its environment. On the other hand, it is not clear that DALM may emit photons through a direct effect of electromagnetic fields. This computational chemistry effort was undertaken to help explain the thermal and field sensitivity, if any, of DALM and related molecules. This computational chemistry effort considered the possibility of direct nonlinear electromagnetic field effects on molecular events in biological electron transfer systems.

1.2 Approach

Conceptual MindWorks, Inc. (CMI) conducted this research effort to explore the issues surrounding luminescence in DALM. The focus of this fundamental, mechanistic research was the development of an integrated theory-experimental model for the luminescent properties of DALM when subjected to perturbing electric and magnetic fields. This effort incorporated the fields of traditional computational chemistry, biophysics, and mathematical simulation.

The effort was accomplished by one project specific research scientist on site at Brooks AFB (Dr. Katrina Wagner-Brown) who performed computational chemistry research, augmented by one technical resource (Dr. Kim Ferris, Pacific Northwest National Laboratory) experienced in electronic structure investigations optical properties, and free radical chemistry from both theoretical and experimental viewpoints, and program management oversight (Dr. George Irving). Collaboration was maintained between experimentalists and modelers, particularly since detailed

structural information on DALM was not available. A three phased effort was envisioned to resolve the experimental question. 1) Construction of a data base containing theoretical and experimental information related to luminescence; 2) Development of static models for DALM (ground state structure and various excited state electronic structures) to identify the more probable sources of high luminescence yields and how energy is moved through the molecule; and 3) Development of computational machinery for studying the effects of electric fields on the structure of DALM. CMI scientists suggested experiments to enhance this effort, in particular for defining the spectral and kinetic relationships necessary for the model. CMI held two seminars per year on progress of the work, made several presentations in national scientific forums, and published research results in peer-reviewed journals.

The research outlined above had a theory focus on the structure and dynamics of DALM. The approach was expected to identify fundamental chemical and physical mechanisms of the radiofrequency response of DALM to microwave energy. Analytic work was performed to verify the computational work.

1.3 Recruitment

Four and one half months were required to recruit and hire the scientist for this task. Ads were placed for the required Physical Chemist in Chemical and Engineering News, The Journal of the Society for Applied and Industrial Mathematics, the office of the National Academy of Sciences, National Research Council Fellowship Program, and several Internet bulletin boards (American Institute of Physics and the Computational Chemistry Archives). Senior individuals in industry and institutes of higher learning were contacted personally by Drs. Kim Ferris and George Irving with information on the qualifications of the scientist required in this effort. 40 applications were received for the physical chemist position. This relatively low number of applications was attributed to the highly specialized nature of the work required. CMI developed a written process for evaluation of the candidates. Following several reviews of the applicants and several telephone interviews, one applicant was invited to present a seminar at Brooks AFB. Dr. Katrina Wagner-Brown, a recent Ph.D. from Vanderbilt University, traveled to San Antonio during the first week of October 1996. She presented a seminar for the HED (formerly AL/OES and AL/OER) audience on October 3rd. Following the seminar she talked with many of the scientists, toured the facilities at building 175E, and Brooks AFB. Ms Elaine Mendoza, President and CEO of Conceptual MindWorks, Inc., and Dr. George Irving, of CMI interviewed Dr. Brown. She returned to Nashville on October 5th. Following discussions with Dr. Albanese and Dr. Kiel of HED (formerly AL/OE) and Dr. Kim Ferris, PNNL, CMI decided, on October 7, 1996, to offer the Physical Chemist position to Dr. Brown. Dr. Brown accepted the position on October 10, 1996. She reported for work on November 19, 1996. The other 39 candidates for the position were sent declination letters. Most of these were sent during the first two months of recruiting. The

individuals in the zone of selection were informed after Dr. Brown accepted the position.

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1.5 Reports

Monthly status reports were provided during the course of this effort. Dr. Brown presented seminars for the scientific staff of AFRL/HED two times per year. She presented papers at approximately two scientific meetings per year. One paper was published in the Materials Research Society Symposium Proceedings, Volume 488, 1998 and several other publications are in the stages of final editing for publication.

1.6 Executive Summary

The Directed Energy Bioeffects Division, Human Effectiveness Directorate, Air Force Research Laboratory, Brooks Air Force Base, TX has developed a chemical, diazoluminomelanin (DALM). The luminescence of DALM increases when irradiated by electromagnetic fields. The luminescence appears to be directly proportional to the temperature of the medium within which the molecular species resides, but the luminescent response is also a function of other medium properties such as salt content and excitation energy. DALM may be a prototype polymeric material in a dosimeter for microwave radiation. On the other hand, it is not clear that there is a direct relationship for DALM and electromagnetic field stimulated photon emission. This computational chemistry effort was undertaken to help explain the thermal and field sensitivity, if any, of DALM and related molecules. This effort considered the possibility of direct nonlinear electromagnetic field effects on molecular events in biological electron transfer systems.

Conceptual MindWorks, Inc. (CMI) conducted this research effort to explore the issues surrounding luminescence in DALM. The focus of this fundamental, mechanistic research was the development of an integrated theory-experimental model for the luminescent properties of DALM when subjected to perturbing electric and magnetic fields. This effort incorporated the fields of traditional computational chemistry, biophysics, and mathematical simulation. Collaboration was maintained between experimentalists and modelers, particularly since detailed structural information on DALM was not available.

The electronic structure of the proposed poly-tyrosine backbone of DALM is comparable to phenol oligomers and forms representative basis for its backbone response. The electronic structure depends strongly on the torsion angle between the neighboring phenyl rings and this relationship was explored through several methods. Torsion potential curves of 1,1'-dihydroxybiphenyl have shown an interdependence between the hydroxyl groups and the ring torsion orientations. Additionally, the potential curves as well as molecular dynamics simulations have shown that neighboring rings in the poly-phenol system fluctuate relatively freely around the angle found in the minimum energy structure. They are unlikely to become co-planar where the electrons would be the most delocalized and the electronic excitation energies the lowest and thus there is a steric control aspect to its electronic properties. Studies of longer phenol oligomers have shown that neighboring rings in the chain are relatively unaffected by monomers further away and the oligomer behaves as a series of 1,1'-dihydroxybiphenyl moieties.

The properties of anionic phenolic oligomers were also examined due to the acidity of the phenol hydroxyl group. Torsion potential curves and molecular dynamics of these systems show there is less freedom in the rotations of the rings and the system is still unlikely to become planar at room temperature. The anionic phenols, however, have lower electronic excitation energies than the neutral oligomers and show more overlap with luminol transition states.

Although the electronic properties of both the backbone and luminol in DALM were studied, there are still several more analyses that need to be done to establish the

fundamental mechanism of action and may affect its application in device development. The research team that performed these studies is eager to study the effects of pH on the system in addition to further studies on the effects of solvent. All of the electronic properties of these systems also need to be reexamined in the presence of an electric field.

2.0 SECTION II

2.1 Objective

The objective of this research was to develop a physical model for the luminescent properties of DALM and like molecules subjected to perturbing electric and magnetic fields. At the start of this project, detailed information about the electronic origins of luminescence in these systems had not been developed. In this effort, we have identified key characteristics, proposed several physical mechanisms for the luminescence of DALM, and have assessed key physical characteristics, which would allow for mechanistic interpretation of experimental measurements.

2.2 Phenolic Oligomers

2.2.1 Development of the phenolic model for the electronic properties of DALM

From the onset, detailed experimental information was not available for the molecular structure of DALM, however; luminescent measurements on a series of samples of controlled composition have suggested that the DALM system has a polytyrosine backbone with associated luminol moieties. The luminol may be attached to the polymer backbone in either a covalent bond or a drug-receptor type interaction, although it is not an absolute requisite for luminescence in this system. In fact, phenol itself demonstrates prolonged phosphorescent behavior when compared to other conjugated ring systems such as naphthalene. DALM itself can be prepared either biosynthetically or by conventional chemical synthetic techniques such as diazotization.

Thus, the polytyrosine system was used as the starting point for the theoretical treatment of the DALM. The proposed backbone, shown in Figure 1, bears a strong resemblance to the phenyl oligomeric units of the conjugated polymer poly (p-phenylene), PPP. In general, energy in conjugated conducting polymers can move by charge transfer and may be transferred to a dopant from the backbone. These mechanisms of energy transfer, present in similar systems, suggest that the luminescence in DALM is due to an excitation of the backbone with subsequent energy transfer to the luminol.

Given this hypothesis, a series of electronic structure calculations were performed to determine the electronic manifold for a model backbone system. Electronic transition energies for excited singlet and triplet states of tyrosine were evaluated using the AM1 Hamiltonian with configuration interaction allowing multiple excitations (MECI) in MOPAC93. In order to determine the trends in excitation energies for more extended systems; electronic transition energies were determined as a function of oligomer length. Figure 2 shows the singlet excitation energies for tyrosine oligomers containing 1 to 3 monomers. Phenolic oligomers, shown in Figure 1b, were also examined for the potential that these simpler systems would behave in a representative manner of the polytyrosine system, but without the additional complications created by the longer and more complex side groups. Singlet and triplet electronic transition energies for phenolic oligomers containing 1 to 5 monomers are

shown in Figure 3a and b. Combined, Figures 2 and 3 show several trends in the transition energies of the phenol and tyrosine systems: for both systems the transitions to lower energy excited states are more probable for longer lengths of oligomer (indicating that the longer oligomers could be more easily excited) and there are more excited triplets with large oscillator strengths as the oligomer length increases.

Figure 4 shows the band gap (estimated as the difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)) for the phenol and tyrosine oligomers as a function of inverse oligomer length. The band gap decreases with oligomer length and approaches 7.75eV for the phenol oligomers and 7.69eV for the tyrosine oligomers. While these energies are consistent with each other, they are obviously too high as is normally observed by SCF level Hartree-Fock calculations. Figure 5 shows the excitation energies of two states in the phenol and tyrosine oligomers as a function of length. The higher energy points are derived from the strongest excitation in the system and the lower energy points from the first excitation. The intersection of the trend lines indicates that the relative importance and strengths of the different excitations may change as the length of the oligomer changes. The energy of the first excited state in tyrosine approaches 3.47eV as the oligomer length increases and in phenol the energy of the first excited state approaches 3.76eV. These similarities in the phenol and tyrosine oligomers suggest that there are similar electronic processes occurring in the two systems and indicate that the phenol oligomers will make a reasonable approximation to the tyrosine backbone.

Orbital amplitude plots for phenol and biphenol (1,1'-dihydroxybiphenyl, hereafter referred to as BP), shown in Figure 6, indicate that the HOMO is π -like and the LUMO is π^* -like as is seen in many conjugated polymers. The charge density in BP shows limited conjugation due to the nonplanar arrangement of the phenyl rings. An electronic excitation involving the HOMO and LUMO orbitals (a $\pi - \pi^*$ transition) would create a charge transfer across the rings since the orbitals are localized on different rings. If the rings were coplanar there would be more efficient conjugation, and the charge localization would be diminished. This can be easily seen by examining the orbital amplitude plot for the HOMO of BP in a coplanar conformation as shown in Figure 7. In Figure 8, The dependence of the HOMO-LUMO gap on the torsion angle between the rings in BP is shown. Similar trends are seen in the excitation energy of BP as a function of torsion angle (Figure 9). Based upon the above results, it was viewed that the polyphenolic system acted as a representation model for the polytyrosine system. Subsequent modeling studies have used phenolic oligomers as the basic model unit.

2.2.2 Interring torsion potential for 1,1'-dihydroxybiphenyl (BP)

The obvious effects of the torsion angles between the rings on the electronic structure force us to consider which conformations are preferred for the polymer backbone. We have found that the orientations of the hydroxyl groups on the phenyl rings have a strong influence on the conformation and torsion angle of the system, and, in particular, different hydroxyl group orientations, shown in Figure 10, give rise to

five minima in the energy surface of BP. There is a single minimum in the torsion potential curve for the cis conformation, and double minima for the trans and head-to-tail conformations. The lowest energy conformation occurs when the hydroxyl groups are pointed in towards one another (cis) and in this conformation the torsion angle between the two phenol rings is predicted to be around 100° by ab initio methods and 60° by semi-empirical and molecular mechanics methods. If the hydroxyl groups on BP are both oriented outwards (trans) the preferred torsion angle is slightly larger and the system is in its highest energy minima. An intermediate energy minima occurs when hydroxyl groups on neighboring rings are pointed in the same direction (head-to-tail), giving rise to a torsion angle predicted to be approximately 60° by all methods.

Geometry optimizations of head-to-tail phenol oligomers containing 2 to 5 monomers, using the AM1 Hamiltonian, show that the torsion angle between neighboring rings is around 55° as it is predicted to be in head-to-tail BP. However, when the system is in an excited state long enough to relax its geometry one of the torsion angles is smaller (see Table 1) indicating that excitations in the system may alter the geometry and modify the amounts electron delocalization.

Given the strong dependence of the electronic properties of the system on the torsion angle, we must consider whether the system spends the majority of its time in the optimized conformation or whether there is enough variance in conformation over time that time-averaging of the electronic properties is needed. To address this issue, we have calculated the heats of formation for the BP system as a function of torsion angle to determine barriers to ring rotations, and have subsequently performed molecular dynamics simulations to observe conformational changes over time.

The torsion potential curves for the 3 minimal energy conformations of BP were calculated using the AM1 and PM3 Hamiltonians, the MM+ and MM3 force fields, and the 6-31G* and 3-21 ab initio methods. The torsion angle between the two phenols was varied through 180° and the resulting dependence in the heat of formation on the angle is shown in Figure 11 for the MM3, 6-31G* and AM1 methods. The PM3 Hamiltonian, MM+ force field and 3-21G ab initio methods gave unphysical results and were inconsistent with the other methods so their predicted curves are not shown. The 3-21G basis set has shown a tendency to overestimate proton acceptor interactions in hydrogen bonds and the PM3 Hamiltonian has failed to reproduce ab initio results on similar systems. The deviations of these methods from the 6-31G* ab initio results is likely due to the need for a better descriptions of intramolecular hydrogen bonding and repulsion forces.

All remaining methods predict large peaks in the energy at 0° , where the OH's are both on the same side of BP, and 180° where the OH's lie opposite one another. The height of the barriers for the geometries occurring at 0° and 180° , at least 10 kcal/mole, are sufficiently large that the rings will not tend to be coplanar, and it is unlikely, at room temperature, that the system will often pass through these configurations. Notably, we have encountered five minima in our investigation of phenol rotation angle by the ab initio methods, as seen in Figure 12a. These minima have been characterized by frequency analysis to have no negative frequencies. The

absolute minima is obtained for a cis conformation (for every method used) and the relative energies of the five conformations are given in Table 2.

The optimized structural parameters for the five lowest energy conformations of BP are given in Table 3. The MM3 technique yields larger bond lengths for all three conformations (except in the case of the C-O bonds) displaying the methods' difficulties in accounting for electron delocalization. On the other hand, the AM1 calculations predict small inter C-C bonds when compared to other methods. The AM1 method also predicts that the hydroxyl hydrogens will be 8°-10° out of the ring plane for each conformation. In the head-to-tail conformation, however, the AM1 method predicts the smallest average deviance from the ring plane for the two hydrogens. For this conformation, all of the other methods also predict at least one of the hydrogens to be substantially out of the plane (by over 40° in the ab initio calculations). In all cases, regardless of the degree to which the hydrogen is out of the ring plane, the hydroxyl oxygen is at most only several degrees out of the plane.

Although all of the methods employed predicted the absolute minima to be the cis type conformation, the structures of the rotational potential curves found using the ab initio methods were not completely reproduced by the semi-empirical methods nor molecular mechanics, as can be seen by comparing the plots in Figure 12. The ab initio 6-31G* results (Figure 12a) show distinct torsion potentials for each of the cis, trans, and head-to-tail conformers with small barriers to the coplanar conformations. Ring rotations for the trans and head-to-tail conformations encounter a small barrier, located at 90°, suggesting its source is the loss of π conjugation. The MM3 method had difficulty reproducing the peaks at 90°. Although the method did predict two minima in both the trans and head-to-tail curves, the second minima in both curves were negligibly small (Figure 11c). The MM3 technique also predicted energy differences between the curves for the various conformations to be about half as large as the differences found in the other methods, as can be seen in Table 2. The AM1 calculations showed five minima but predicted a small 90° barrier for the cis conformation (Figure 11b) while showing an asymmetry around 90° but no peak for the trans conformation. Both the AM1 and MM3 methods predicted the absolute minimum in the trans rotational curve to be near 140° whereas in the 6-31G* curve, the 140° minima is slightly higher in energy than the 65° minima. A qualitative accounting of the pathological tendencies by these methods would lead to the 6-31G* description.

The sizes of the energy barriers at 90° vary from conformation to conformation and are dependent upon the method of calculation. The 6-31G* studies predict no barrier for the cis conformation ranging to a 1.3 kcal/mol barrier for the head-to-tail conformation. The AM1 barriers are from 0.7 kcal/mol for the cis conformation and 1.4 kcal/mol for the head-to-tail conformation. The MM3 barriers are the smallest; about 1.0 kcal/mol for both the head-to-tail and the trans conformations. Predicted barriers for the perpendicular conformation of biphenyl are 1.5-1.6 kcal/mol, higher than those observed here. The calculated energy barriers to coplanarity in the BP system, ranging from 10-12 kcal/mol, are much higher than the 3.2-3.2 kcal/mol

barriers seen in the biphenyl indicating that the hydroxyl groups have a large influence upon the steric interactions of the system.

Variations in the torsion angle of BP also produce small changes in the geometry of the system. There exists a correlation between the interring bond length and the angle as shown in Table 4, the features of which are independent of the method used for the calculation. For each of the three conformations there are two minima in the bond length as a function of torsion angle. One minima occurs for a conformation with a torsion angle within several degrees of 45° and the other for a conformation with a torsion angle within several degrees of 135° ; thus the shortest bond length occurs for a conformation having a torsion angle near, but not at, the angle for which the energy is a minimum. The bond length increases by 0.003 \AA to 0.02 \AA towards 0° and 180° , where the steric interactions are the greatest. Likewise, it increases by a smaller amount as the angle approaches 90° . The two local minima in the bond length appear even when the torsion potential curve produced only one minima in the energy, as in the case of the 6-31G* cis curve. There is also a correlation between the average C-C bond length within the rings and the torsion angle, the qualitative features of which are also independent of the theoretical method used. This bond length is a minimum, regardless of conformation, at around 90° and increases by 0.002 \AA to 0.004 \AA as the molecule approaches either of the co-planar configurations.

2.2.3 Phenol hydroxyl group rotation

While previous investigation at SCF and correlated levels of the phenolic OH group rotational barrier have found it to be a 2.4-3.4 kcal/mol surmountable barrier, the situation for the BP system is different in that a hydrogen bond needs to be broken to allow for OH group rotation. To examine how easily the BP system can change from one hydroxyl conformation to another, we have examined the barrier to the rotation of a hydroxyl hydrogen in BP with the 6-31G* method. The two geometries corresponding to the two energy minima of the 6-31G* head-to-tail potential curve were used as starting points. For both conformations, the hydrogen of the more planar hydroxyl group was rotated 180° from its starting torsion angle near 180° to a final torsion angle of 0° at which the conformation has been converted to a cis structure. While we would have preferred to use a partially frozen geometry to reduce the degrees of freedom and computational effort, the larger differences in the interring torsion angles (ϕ) for the different conformations required a more relaxed geometry optimization. Figure 12 shows the energy of these two systems as a function of the OH torsion angle. The energy barrier at 90° , for both conformations, is asymmetric with a higher energy barrier in going from the cis to the head-to-tail conformation. There is a 1.2 kcal/mol barrier for the conversion of the minimum energy head-to-tail structure to cis but a 3.1 kcal/mol barrier for the reverse transformation. Similarly, there is a 2.2 kcal/mol barrier in converting the higher energy head-to-tail conformation to a cis structure but there is a 5.3 kcal/mol barrier for the reverse.

Figure 13 shows the torsion angle between the phenol rings as a function of the torsion angle of the hydroxyl group for the same two 6-31G* head-to-tail minimum

energy conformations. The lowest energy conformation in the head-to-tail type structure has a ring torsion angle of 55° while the second minimum energy conformation has a ring torsion angle of 113° . As the hydroxyl group is being rotated, the structure is changing to a cis conformation for which the torsion angle at the minimum energy conformation is 106° . The ring torsion angle of the second energy minimum should then be expected to change only by a small amount as the hydroxyl group rotates, as Figure 13 confirms. The lower energy conformation, however, upon the hydroxyl group rotation, evolves from a ring torsion angle of 55° to 105° . Interestingly, the ring torsion angle in this case does not significantly change until the hydroxyl group has rotated by 130° , well past the 90° barrier where the system has converted to the cis conformation.

2.2.4 2,5-di(2-hydroxyphenyl)phenol (TP) conformations and relative stabilities

The overall closeness of the energies and shallowness of the rotational barriers for the three conformations does not allow us to preclude any of the conformers and the situation becomes less clear when we consider the dynamics of conformation interconversions and models for larger oligomers. In Figure 14 we give four 2,5-di(2-hydroxyphenyl)phenol (TP) examples where the conformational questions appear more complex. Based upon the relative stabilization energies (Table 2) for the BP system, the lowest energy TP conformer would be expected to display a head-to-tail and a cis interaction (since a cis and a cis interaction would be impossible for the system to obtain). As can be seen in Table 5, which shows the relative energies of the TP conformations, the cis, head-to-tail is in fact the lowest energy conformer. It is interesting to note that in all the TP conformations, the torsion angles between the rings are within several degrees of the torsion angles found for the optimum geometries of the individual BP's with the same hydroxyl orientations. Through comparisons of Tables 2 and 5, one can also see that the energy difference between any two TP's is similar to the energy differences between the component BP's. For example, the AM1 energy difference between the cis, trans and cis, head-to-tail TP's (the third and first entries in Table 5) is about 1.8 kcal/mol. This is close to the 2 kcal/mol difference there would be between systems of two BP's, one system having one cis and one trans BP, and the other system having one cis and one head-to-tail BP.

All of the TP configurations shown in Table 5 have torsion angles corresponding to the torsion angles that occurred for the absolute energy minima in the constituent BP's. There is also, however, a minima in the energy of the TP system if the constituent BP's have torsion angles that correspond to local minima in the BP torsion curves. For example, the 6-31G* torsion curve for the head-to-tail BP conformation shows two minima, one occurring for a torsion angle of 55° and one for a torsion angle of 113° . The cis, head-to-tail TP in Table 5 shows the energy for the TP when the head-to-tail portion has a torsion angle of 55° . There is also a stable geometry, with an energy about 1.7 kcal/mol higher, for the cis, head-to-tail TP where the head-to-tail portion has a torsion angle of 115° . This 1.7 kcal/mol energy difference between the two TP's is close to the 1.2 kcal/mol difference between the two minima in the head-to-tail BP conformation (see Table 2). In other words, neighboring phenols in

a TP behave very much like their BP equivalents. Both this and the discussion above seem to indicate that neighboring phenols in the TP are only slightly influenced by the third phenol and behave very much like a BP would which simplifies the study of the longer length oligomers.

2.2.5 Predicted electronic absorption spectra for phenolic oligomers

The predicted absorption spectra for phenol oligomers of varying lengths are shown in Figure 15. The energies were calculated for singlet states using the ZINDO/S Hamiltonian with configuration interaction using single excitations. In general, longer oligomers resulted the more activity there is in the higher energy region. None of the oligomers, however, show any significant absorption beyond about 290nm. In general, the predicted spectra show good agreement with experimental spectra for phenolic systems, with the exception of an electronic absorption in the 300-350 nm region. This additional peak was observed through luminescence measurements, and had no corresponding electronic absorption in the neutral phenolic results.

The three different conformations of BP have slightly different excited states, as would be expected from the previous discussion of the torsional effects on the electronic structure. The differences in excitation energies for the different conformations produce differences in absorption spectra for the three conformations. Figure 16 shows predicted electronic absorption spectra for each of the 5 minima found in the three torsion potential curves. Experimentally, the energy differences between the different conformations should result in a temperature dependence of the absorption spectra with more contributions from the trans and head-to-tail components at higher temperatures. We can examine the relative contributions to the absorption, by the different conformations, through molecular dynamics simulations of the system which will show which conformations predominate.

In a preliminary examination of solvent influences on the electronic structure, we have also performed AM1 configuration interaction calculations (Figure 17) for the cis, head-to-tail and trans lowest energy conformations both with and without solvent (COSMO). There is little difference in the energies and strengths of the lower energy transitions in the presence of the solvent and only small differences for the trans and head-to-tail higher energy processes. These small differences are viewed with caution due to the incomplete representation by which COSMO handles solvation interactions.

2.2.6 Molecular dynamics simulations of 1,1'-dihydroxybiphenyl (BP)

The MM3 force field in the TINKER molecular modeling program contains molecular dynamics modules for the simulation of the dynamic properties of molecules and molecular mechanics modules for structural minimizations. Included with this program are a number of commonly used force fields which have been parameterized for large classes of molecules. One of the earlier, more general force fields developed by Allinger was the MM2 force field, which has been subsequently superseded by the more accurate MM3 method. Wanting to extend our interpretation of the phenolic properties beyond the static picture of electronic structure calculation we needed an accurate representation of the torsional potentials we had earlier described. In

comparing the MM3 force field with the 6-31G* ab initio method (Figure 11) we noted significant deviations in relative minima and energetics. We have, therefore, engaged in an effort to reparameterize the MM3 force field to better reproduce the ab-initio BP results, which in turn, would enable us to run dynamics simulations with more trustworthy results. The MM3 parameters controlling the strength of the hydrogen bonding interaction between the hydroxyl hydrogens on one ring with the hydroxyl oxygens on a neighboring ring have been increased but the distance of the bonding interaction has been decreased. The van der Waal radii of the hydroxyl hydrogens has been increased and the strength of pi-bonding interactions among the carbons has been increased. These properties all affect the shapes of the BP torsion curves. The MM3 parameter controlling the interaction distance between hydroxyl hydrogens on one ring with the inter-ring linking carbon on the second ring has been decreased (the effects of the hydrogen overlapping with the pi-cloud are increased). This change along with the changes in the hydrogen bonding interaction between the hydroxyl hydrogens and neighboring ring hydroxyl oxygens, controls the magnitudes of the torsion potential curves. Corresponding ab initio 6-31G* calculations were performed to illustrate the electron density deformations for the hydroxyl group interacting with the phenyl p system. As shown in Figure 18, there is little distortion. The resulting reparameterization gave good agreement with the ab initio results, although it was at the cost of general applicability.

Figure 19 shows a 50ps molecular dynamics simulation, at room temperature, using the reparameterized MM3 force field for a 4 phenol oligomer: the three torsion angles between the rings have been graphed versus time. It can be seen that while the rings will periodically pass through the perpendicular configurations they never become planar with one another. In fact, for the majority of the time the torsion angles between the rings are the close to the angles corresponding to the lowest energy head-to-tail and cis conformations. Neighboring rings can only be found in trans conformations about 5% of the time, a percentage that should increase if the temperature of the simulation is increased. The simulation also demonstrated the coordinated motion of the OH group in changing from a head-to-tail conformation to a cis conformation: that is, the positions of the hydroxyl hydrogens do not control the torsion angle but rather the torsion angle influences the positions of the hydroxyl groups. In other words, when the hydroxyl group goes trans, the torsion angle does not automatically jump to the preferred angle (angle at which the energy minima occurs) of the trans conformation. These results further buttress earlier results that due to the presence of multiple oligomer conformations that can persist due to intramolecular stabilization, models for DALM behavior need to include the flexibility for structural diversity and dynamical behavior.

2.3 Anionic Phenol Oligomers

2.3.1 Acidity and stability of anionic phenols

Investigations to this point have been on neutral phenolic oligomers although there is sufficient experimental evidence on the acid properties of phenol and tyrosine.

Given the potential for a stabilizing influence by longer phenolic oligomers for the anionic species through conjugative effects, we have also examined the properties of phenolate oligomers. Starting from an ionized phenolic unit, we have constructed two model systems to explore the effects of an acid reaction on the DALM phenolic polymer. In the first, a proton is lost from the terminus of the head-to-tail conformation of the phenolic polymer as shown in Figure 20a. This model was constructed to examine the effects of end-group ionization and the extent along the polymer backbone that was affected by the ionization. The second model (double-sided), shown in Figure 20b, is used to explore mid-chain ionization.

Table 6 gives the heats of formation for single-sided stabilized phenolate oligomers (end-group ionized) in both the gas and solvated phases (COSMO) as calculated using the AM1 Hamiltonian. As should be expected, the addition of solvent lowers the energy of the systems. Table 7 shows the heats of formation for double-sided stabilized phenolate oligomers (mid-chain ionized) in the gas phase. For double-sided and single-sided anionic systems with the same number of rings (e.g. the single-sided phenolate oligomer with 2 neighboring rings and the double-sided phenolate oligomer with 1 neighboring ring on either side) the energy is lower for the double-sided system. This additional stabilization is due to the additional hydrogen bonding interaction. In the double-sided conformations there are two hydrogens pointing towards the available oxygen whereas in the single-sided conformation there is only one hydrogen pointing towards the available oxygen, making the former case more stable.

The proton affinities, calculated using the calculated values for the heats of formation of the neutral and anionic oligomers and the experimental gas phase number for the hydrogen ion, are shown in Table 8 for single and double-sided oligomers. The proton affinities tend to decrease with the length of the oligomer and are larger for the single-sided oligomers where the anionic oxygen is only interacting with one hydrogen. This decrease in proton affinity with length indicates longer oligomers will tend to be more acidic. In general it is seen that the single-sided phenolate oligomers are less stable than the double-sided. The additional complexity of the polymeric system should reflect the effects of the single and double donor systems. As such, the general trends towards greater acidity should make the presence of phenolate anions a distinct possibility, and should be included in prospective models of DALM behavior.

2.3.2 Effects of hydroxyl group ionization on the torsional potential of BP

Figure 21 shows the torsion potential curves for a head-to-tail BP and the head-to-tail phenol anion found from AM1 calculations. In the case of the anion, there is still a barrier at 90° however the relative depths of the minima on either side have changed: the minimum near 50° has become 2 kcal/mol more negative than the 140° minimum. This change presents a larger barrier that must be overcome in going from lower torsion angles through the 90° conformation (about 3.5 kcal/mol). In addition, the global minimum has shifted to a slightly lower angle than it was in the neutral-charged BP. The barriers to the coplanar conformations are fundamentally the same for the neutral-charged and anionic oligomers. Essentially, the attraction between the anionic oxygen and the hydroxyl hydrogen on the neighboring ring has lowered the

torsion angle of the system and made it more difficult for the rings to shift their relative positions toward the perpendicular conformations. These differences between the neutral and charged systems are evident in the molecular dynamics simulations and change the conformation dynamics of the phenolic material.

2.3.3 Predicted electronic spectra for anionic phenolic oligomers

The anionic phenol species is a distinctly different electronic structure species. Figure 22 shows the predicted absorption spectra for end-ionized anionic-charged phenolic oligomers. When this spectra is compared to that of the neutral oligomers (Figure 15) it can be seen that the anionic spectra demonstrate character of both the neutral phenol species and the phenolate anion. Notably, the distinct phenolate features are electronic absorptions at wavelengths greater than 300nm. Examinations of DALM emission spectra indicate that electronic absorptions in the 290nm to 350nm region provide an energy source for luminescence. The absorption spectra of the anionic oligomers in these same energy regions suggest that these processes be identified as primary candidates for the energy transfer for the DALM emissions, and should be additionally qualified for energy coupling to luminol.

2.3.4 QM/MD simulations of neutral and anionic phenolic oligomers

In order to investigate oligomer dynamics for the neutral and anionic systems, the next task was to again reparameterize the MM3 force field to reproduce the characteristics of the phenolic anion torsional potentials. In view of the potential role of the torsional angle for stabilizing the anionic species through conjugative effects, it was viewed that the MM3 method could be insufficient to handle these electronic factors. Therefore, we have performed a series of QM/MD simulations in which the intramolecular interactions and forces are evaluated in an electronic structure manner, and the nuclear motions are handled classically. Simulations of neutral and phenolate oligomers were performed in the HyperChem program using the AM1 Hamiltonian.

Sampling individual snapshots of the molecular dynamics trajectory, structural parameters reflecting the interring torsion flexibility and dynamics were developed. Table 9 gives the static and dynamic torsion angles between phenol rings in neutral-charged oligomers. Given the averaging behavior the dynamic values, one should not overinterpret the torsion angles. For example, in the dynamic picture, equal populations of angle x and angle $-x$ result in a time averaged value of zero although the sample species may never reside at that value. Given that frame of reference, the static angles are taken from the optimized geometries of electronic structure calculations and the dynamic angles are from a 20ps simulation with a 2 ps equilibration interval, constant $T=300K$. The large standard deviations from the mean torsion angles in the dynamics simulations indicate that the rings have considerable freedom in their movements. Table 10 gives the static and dynamic torsion angles between rings in anionic-charged phenolic oligomers. The deviations from the mean angles are much smaller for the anionic systems are stiffer and the rings do not rotate as freely as in the neutral oligomers.

Statistical values did not adequately represent the differences between neutral and anionic species, and snapshot movies of the dynamics trajectory were created to illustrate molecular motions. Broad rotational motions for the hydroxyl groups were seen for the neutral oligomer. The dynamics trajectory of the anionic species demonstrated several examples of altered interactions with restricted motions. The focal point of the restrictions was the anionic oxygen – the site which lost an acidic proton. The hydroxyl group on the adjacent phenyl ring invariably points its hydrogen towards the anionic hydrogen, even with phenyl-phenyl torsion changes. Secondly, interconversions among the cis, trans, and head-to-tail interactions were limited as the hydroxyl groups neighboring the acidic phenol site became more involved in hydrogen bonding to the anionic site rather with other potential partners. Last, as the dynamics of the phenyl-phenyl torsional angle were altered compared to the neutral species, predictions of the electronic spectra need to reflect these differences. As such, the presence of acidic sites which can lose protons could have profound effects on the structural dynamics and electronic properties of the phenolic polymer.

2.4 Potential Role of Luminol in DALM Luminescence

The exact role of luminol in DALM luminescence at this point is still unclear. The presence of luminol has definitely been shown to have an enhancing effect on luminescent yield, although its structural attachment to the biopolymer is still unresolved whether it is covalent or a general drug-substrate binding. Although there have been numerous investigations on the luminescent processes in luminol, the majority of previous efforts have focused on the chemical aspects. There is the additional complication that specific molecular structures which would be predominant in solution processes, could have diminished roles in terms of an energy transfer process in DALM.

In an effort to understand the role of luminol in DALM luminescence, we have started from the solution aspects. Electronic structure calculations have been employed to predict the electronic excitation energies for singlet and triplet luminol. Figure 23 shows predicted triplet energies for several forms of luminol which have been proposed to have a role in its luminescence. Most of these forms show transitions around 400-450nm or in the blue region of the visible spectrum. A selected subset of these molecular forms have shown electronic transitions at lower energies (out to the infrared) as shown in Figure 24. These lower energies should be viewed with extreme caution. Given these variations in energies, there are several reaction products in the luminol pathway could be responsible for the emissions seen in DALM. It is suggested that chemical probes with known enhancement or inhibition effects be used to determine the perturbations to the solution response of luminol. In Figure 25 we show the spectra of the singlet and triplet states of luminol (Figure 23b) and a 4 phenol oligomer. There is considerable overlap of the spectral energies for both the triplet and singlet states of the two molecules which would be consistent with a potential energy transfer pathway.

2.5 Computational Methods

The computational chemistry capabilities used to develop the physical models for DALM involved molecular models at several different time and length scales, with varying degrees of computational intensity. There were three primary computational facilities used to support this work: Brooks AFB for local capability, data analysis, and short term molecular dynamics simulations; Pacific Northwest National Laboratories for ab initio and semiempirical electronic structure studies, combined QM/MD simulations, and graphical presentations; and NERSC for electronic structure calculations needed for potential energy surface scans. Simulated electronic absorption spectra were generated using the superposition of Lorentzian profiles with their envelope area scaled to the transition oscillator strength.

There were a number of computational chemistry software packages with varying and complementary capabilities (listed below) which were used to support this effort:

AMPAC, Version 5.0, 5.1 – SemiChem, Shawnee, KS – semiempirical electronic structure (AM1), state importance in configuration interaction

Babel, Version 1.6 – Univ. Arizona – file format translation
 Gaussian92, Gaussian Inc., Pittsburgh, PA. – ab initio electronic structure (3-21G*, 6-31G*), frequency analyses
 Hyperchem Pro, Version 5.0.1 – Hypercube Inc., Gainesville, FL – semiempirical electronic structure (AM1, PM3, ZINDO/S), force field (MM+, AMBER), QM/MD (AM1 molecular dynamic simulations), graphical presentations (orbital amplitude, electron density, animations)
 Tinker, Version 3.6 – Washington University, St. Louis, MO – force field (MM3), molecular dynamics (MM3)
 MOPAC93, Revision 2 – Fujitsu, Inc., Tokyo JP – semiempirical electronic structure (MNDO, AM1, PM3), configuration interaction
 PCMODEL, - Serena Software, Indianapolis, IN – gui data presentation with preliminary structure optimization.
 PC Spartan Plus, Version 1.5; Pro, Version 1.0 – Wavefunction Inc., Irvine, CA – semiempirical electronic structure (AM1), graphical analysis and presentation of electron density
 XMOL, Version 1.1 – Minnesota Supercomputing Center – graphical display
 WinMopac, Version 1998 – Fujitsu, Inc., Tokyo, JP – semiempirical electronic structure (AM1, CNDO/S3, ZINDO/S), solvation models (COSMO, Tomasi)

Public distribution of the software in the above list is restricted by license agreement with the following exceptions. Babel and XMOL are freely distributable and available through several computational chemistry websites. Tinker and GAMESS are web available, but are restricted in that the program authors require notification before use. The remainder have strict user License-fee agreements. Fees are modest. Access and usage was restricted to scientific collaboration through user agreement. General usage and distribution questions should be resolved by conference with the project manager.

2.6 Future directions

While we have studied the electronic properties of both the backbone and luminol, there are a number of areas needing further examinations. At this point we have developed a fundamental basis for structure and electronic excitations in model DALM systems. Its response in the presence of electric fields was the primary motivation for this investigation, and given our basis one should be able to understand how electric field effects perturb the polymer response. Solution effects were handled in only a preliminary investigation. Work in this area usually proceeds best in a effort with strong complementary experimental and theoretical modeling. Further, one cannot say at this point that the DALM system itself represents the optimized set of chemical/physical properties. Once the fundamental action for energy transfer is established, a structure/activity relationship (with chemical derivation studies) should be developed to be able to optimize the system response.

In order to move this work beyond its current limited scope, there are four areas needing attention in the near future: 1) determine the potential role of free radicals on the structural and electronic properties of DALM. Recent structural information

obtained from 2-D NMR experiments has determined the presence of persistent free radicals in the DALM structure. As the reaction mechanism for DALM preparation involves a free radical step, their functionality is unclear. 2) examination of the electronic manifolds of the model polyphenol and luminol system to determine the more probable pathways for energy transfer. Given the vibrational and electronic manifolds for the active species, the formalism for calculation of energy transfer cross-sections can be used to determine more probable pathways. 3) development of a combined chemical and stochastic model which would allow the DALM properties to be used device development. Consistent device performance requires a number of processing variables in addition to the fundamental energy transfer mechanism. For example, one of the primary hindrances for more general application of polyenes is the effect of conjugation and structural defects. Processing and fabrication also introduce a degree of sample diversity which could significantly affect overall performance. 4) investigation of a more complex system of phenolic oligomers and luminol. Real samples are multistrand, have different numbers of repeat units, luminol associated, contained internal water, and are subjected to electric fields. Work to present date establishes a molecular basis, not a materials sciences basis.

2.7 Summary

We have compared the electronic structure of the proposed polytyrosine backbone with that of phenol oligomers and have found that the latter form a reliable representative backbone. In both of these oligomeric systems the electronic structure depends strongly on the torsion angle between the neighboring phenyl rings and we have explored this relationship through several methods. Torsion potential curves of BP have shown that there is a relationship between the orientations of the hydroxyl groups and the ring torsion angle. Additionally, the potential curves as well as molecular dynamics simulations have shown that neighboring rings in the polyphenol system fluctuate relatively freely around the angle found in the minimum energy structure yet they do not become co-planar where the electrons would be the most delocalized and the transition energies the lowest. Studies of longer phenol oligomers have shown that neighboring rings in the chain are relatively unaffected by monomers further away and the oligomer behaves as a series of BP's.

Given the energetically accessible acidity for tyrosine-based ionizations, we have also examined the characteristics of polyphenol anions. Torsion potential curves and molecular dynamics of these systems show there is less freedom in the rotations of the rings and the system is still unlikely to become planar at room temperature. The anionic phenols, however, have lower energy excitation states than the neutral oligomers and would have more overlap with luminol electronic states.

2.8 Tables

Table 1 Torsion angles (°) between neighboring rings in phenol oligomers.

Number of Phenols in Oligomer	Torsion Angle for Ground State	Torsion Angle for Relaxed Geometry of the Ground State's First Excited Singlet	Torsion Angle for Relaxed Geometry of the Ground State's First Excited Triplet
2	56.0	32.9	13.5
3	59.1	51.8	62.6
	58.6	58.8	12.9
4	50.9	51.0	52.3
	51.6	52.2	22.9
	51.1	36.1	51.9
5	51.0	29.6	29.8
	51.9	51.3	52.7
	51.6	51.4	51.9
	51.1	50.9	50.3

Table 2 Relative energies (kcal/mol) for the minima in the BP torsion curves and the torsion angles (°) at which they occur. A dash indicates that a minimum did not occur in the given torsional potential curve.

Conformation	6-31G*		AM1		MM3	
	Angle	Energy	Angle	Energy	Angle	Energy
Cis 1	104.8	0	56.9	0	60.6	0
Cis 2	-	-	120.7	0.0973	-	-
Trans 1	68.3	5.3195	-	-	68.0	2.5495
Trans 2	122.3	5.5435	138.6	4.0183	127.8	1.9648
Head-to-Tail 1	55.0	1.9760	57.1	1.9693	61.7	0.8319
Head-to-Tail 2	113.0	3.1489	130.6	2.5142	110.6	1.5899

Table 3 Parameters for optimized geometries of BP: average bond lengths (Angstroms) and angles (°).

Parameter	Cis			Trans			Head-to-Tail		
	6-31G*	AM1	MM3	6-31G*	AM1	MM3	6-31G*	AM1	MM3
Avg r(C-C)	1.384	1.399	1.400	1.387	1.399	1.399	1.387	1.399	1.399
Avg r(C-H)	1.075	1.100	1.103	1.075	1.100	1.103	1.075	1.100	1.103
Avg r(C-O)	1.347	1.375	1.365	1.351	1.378	1.363	1.358	1.375	1.363
Avg r(O-H)	0.949	0.970	0.973	0.947	0.968	0.972	0.949	0.968	0.973
InterRing r(C-C)	1.499	1.461	1.509	1.494	1.460	1.498	1.496	1.462	1.506
Avg ∠(C-O-H)	110.5	108.6	113.8	110.4	107.8	112.7	110.3	108.2	112.1
∠(C ₆ -C ₁ -C ₇ -C ₈)	104.8	56.9	60.6	68.3	138.6	127.8	55.0	57.1	61.7
∠(C ₅ -C ₆ -O-H)	179.1	189.5	174.9	4.7	8.1	3.4	138.3	169.0	155.7
∠(C ₉ -C ₈ -O-H)	179.1	189.2	174.9	4.7	8.0	3.4	353.3	351.9	358.3

Table 4 Interring carbon-carbon bond lengths for the three conformations of BP (Angstroms). ϕ_1 is the angle, less than 90° at which there was an energy minimum in the torsion potential curve. Similarly, ϕ_2 is the angle larger than 90° where there was an energy minimum in the torsion potential curve. The ϕ_1 and ϕ_2 angles for the particular method and conformation are given in parenthesis beneath the bond length.

	Cis			Trans			Head-to-Tail		
	6-31G*	AM1	MM3	6-31G*	AM1	MM3	6-31G*	AM1	MM3
15°	1.5082	1.4644	1.5175	1.5035	1.4629	1.5077	1.5095	1.4638	1.5128
45°	1.4972	1.4611	1.5088	1.4930	1.4593	1.4980	1.4969	1.4616	1.5051
		1.4614	1.5089	1.4936	-	1.5024	1.4957	1.4620	1.5060
ϕ_1	-	(56.9°)	(60.6°)	(68.3°)	-	(68.0°)	(55.0°)	(57.1°)	(61.7°)
90°	1.4997	1.4636	1.5234	1.4963	1.4633	1.5200	1.4987	1.4638	1.5200
	1.4987	1.4620	-	1.4944	1.4601	1.4980	1.4968	1.4607	1.5071
ϕ_2	(104.8°)	(120.7°)	-	(122.3°)	(138.6°)	(127.8°)	(113.0°)	(130.6°)	(110.6°)
135°	1.4972	1.4610	1.5049	1.4947	1.4601	1.4972	1.4961	1.4605	1.5011
165°	1.5059	1.4635	1.5098	1.5045	1.4638	1.5059	1.5050	1.4633	1.50760

Table 5 Relative energies (kcal/mol) for the four possible TP conformations shown in Figure 15.

	6-31G*			AM1			MM3		
	ϕ_1	ϕ_2	Energy	ϕ_1	ϕ_2	Energy	ϕ_1	ϕ_2	Energy
Cis, Head-to-Tail	103.3	55.0	0	58.9	57.5	0	61.6	63.2	0
Head-to-Tail, Head-to-Tail	54.9	54.5	0.8236	59.1	58.7	1.6139	63.4	62.8	0.9546
Cis, Trans	104.7	68.3	3.1848	57.4	137.8	1.8056	60.3	125.8	1.3566
Head-to-Tail, Trans	56.6	68.6	5.6746	58.3	137.4	4.0697	62.8	124.8	2.5102

Table 6 Heats of formation (kcal/mol) for phenol oligomers and single-sided phenolate oligomers in both the solvated and gas phases.

Number of neighboring phenolic groups	Neutral		Anion	
	Gas Phase	Solvated	Gas Phase	Solvated
0	-22.33	-30.21	-41.05	-117.83
1	-38.65	-51.12	-69.13	-138.63
2	-55.19	-71.50	-89.81	-158.28
3	-71.97	-91.83	-108.19	-178.41
4	-89.06	-112.05	-125.40	-198.47
5	-108.72	-	-141.84	-

Table 7 Heats of formation (kcal/mol) for phenol oligomers and double-sided phenolate oligomers in the gas phase.

Number of neighboring phenolic groups	Neutral	Anion
0	-22.33	-41.05
1	-56.51	-94.33
2	-88.27	-133.80
3	-121.11	-169.36
4	-154.58	-202.94

Table 8 Proton affinities (kcal/mol) for single-sided and double-sided stabilized phenolate oligomers. The proton affinity is given by $\Delta H_f(\text{neutral}) - \Delta H_f(\text{anion}) - \Delta H_f(\text{H}^+)$ where $\Delta H_f(\text{H}^+) = 367.2$ kcal/mol and $\Delta H_f(\text{neutral})$ and $\Delta H_f(\text{anion})$ are the values from Tables 6 and 7.

Number of neighboring Phenolic groups	Single-sided	Double-sided
0	348.48	348.48
1	336.72	329.38
2	332.58	321.67
3	330.98	318.96
4	330.87	318.83
5	334.08	-

Table 9 Static and mean dynamical phenyl-phenyl torsion angles(°) for neutral-charged phenolic oligomers taken from a 20ps molecular dynamics simulation using the AM1 Hamiltonian in HyperChem. (Ph=phenol, h2t=head-to-tail hydroxyl conformation, cis=cis hydroxyl conformation).

Oligomer (Configuration) Ph-Ph	Static		Dynamic	
	Tor0	Tor1	Tor0	Tor1
Ph-Ph	-57.21		Mean	-38.66
			Std. Dev.	48.81
Ph-Ph-Ph (h2t-h2t)	-56.35	56.57	Mean	-96.60
			Std. Dev.	31.47
Ph-Ph-Ph (cis-h2t)	-58.84	-57.46	Mean	-111.63
			Std. Dev.	19.72

Table 10 Static and mean dynamical phenyl-phenyl torsion angles(°) for anionic-charged phenolic oligomers taken from a 20ps molecular dynamics simulation using AM1 Hamiltonian in HyperChem. (PA=phenolate anion, Ph=phenol, h2t=head-to-tail hydroxyl conformation).

Oligomer (Configuration)	Static			Dynamic		
	Tor0	Tor1	Tor2	Tor0	Tor1	Tor2
PA-Ph	-50.42			Mean -51.75 Std. Dev. 9.61		
PA-Ph-Ph (h2t)	-49.72	54.26		Mean -50.95 Std. Dev. 8.69	59.94 16.36	
PA-Ph-Ph-Ph (h2t-h2t)	-49.20	53.88	-56.67	Mean -52.12 Std. Dev. 9.55	91.18 32.89	-86.73 30.82
Ph-PA-Ph	-51.79	-51.83		Mean -52.38 Std. Dev. 6.21	-52.61 6.01	

2.9 Figures

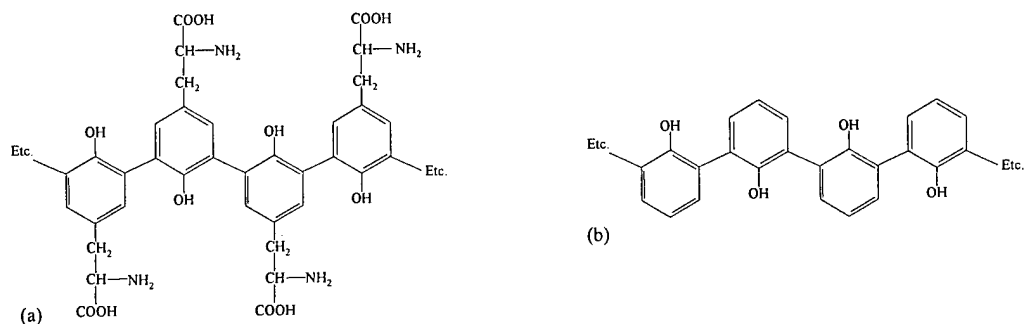


Figure 1 A schematic illustration of the (a) polytyrosine and (b) polyphenol system representing a simplified DALM backbone.

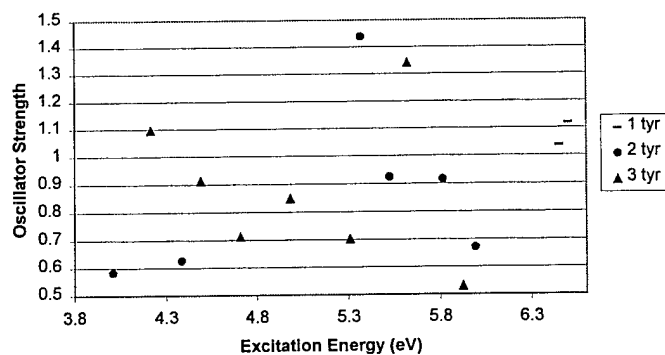


Figure 2 Single excited states of tyrosine oligomers as calculated with the AM1 Hamiltonian and configuration interaction.

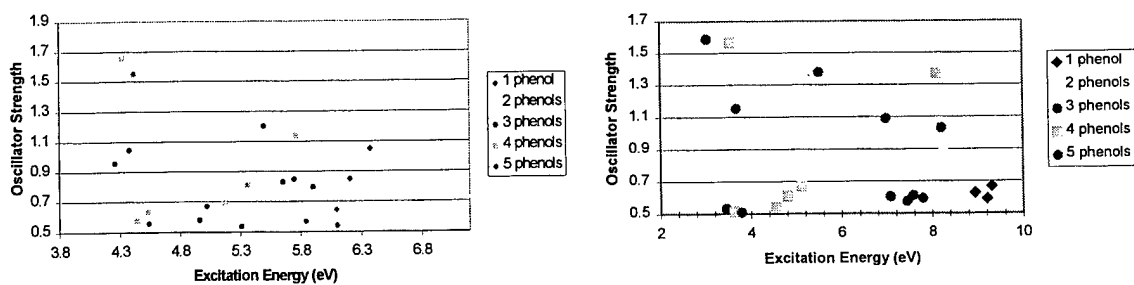


Figure 3 (a) Singlet excited states of phenol oligomers (b) Triplet excited states of phenol oligomers as calculated with the AM1 Hamiltonian and configuration interaction

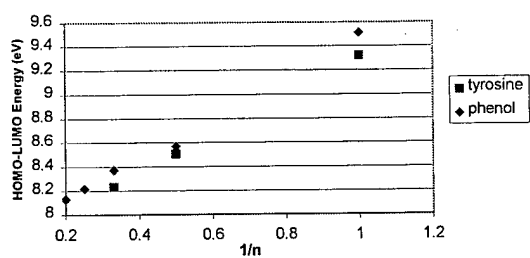


Figure 4 The HOMO-LUMO energy differences for tyrosine and phenol oligomers versus the reciprocal length of the oligomers

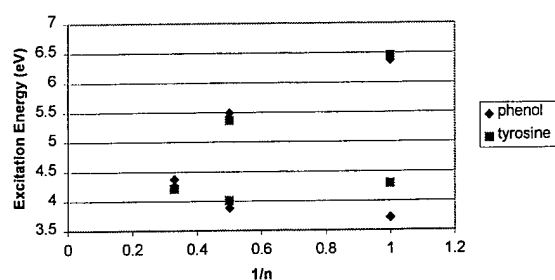


Figure 5 The energies of the lowest energy transition states (lower clusters of points) in phenol and tyrosine oligomers. The higher energy clusters of points are the energies of the first strong transition in the oligomers. All transitions were calculated using the AM1 Hamiltonian with configuration interaction.

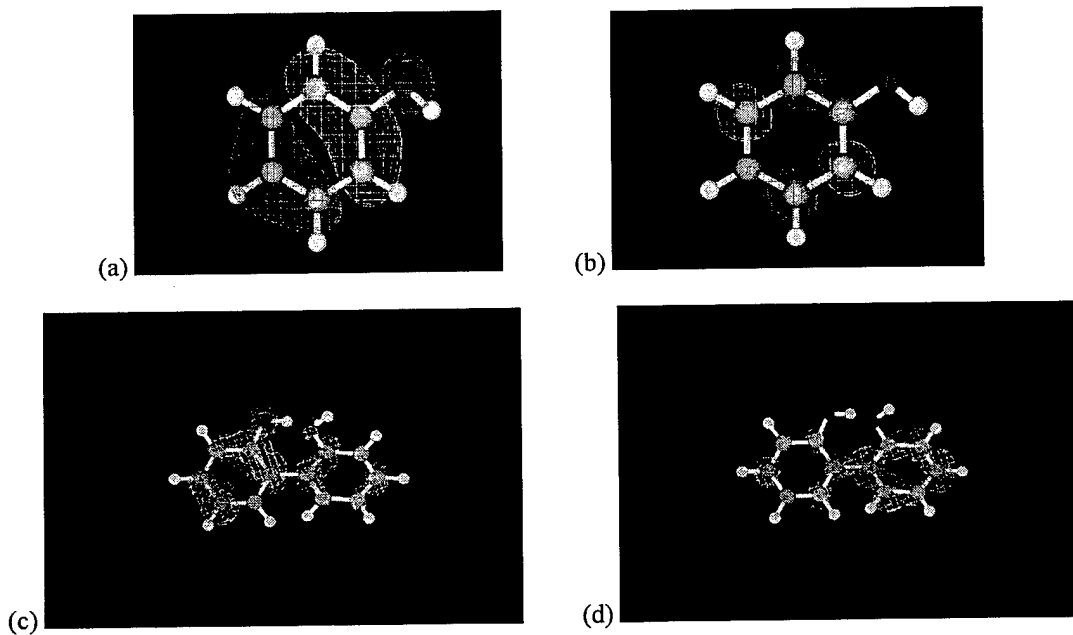


Figure 6 Orbital amplitude plots for phenol (a) HOMO and (b) LUMO, and for BP (c) HOMO and (d) LUMO.

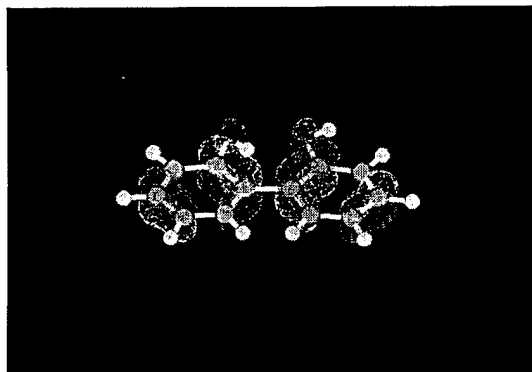


Figure 7 Orbital amplitude plot for the HOMO of coplanar BP showing extensive delocalization over both phenol rings.

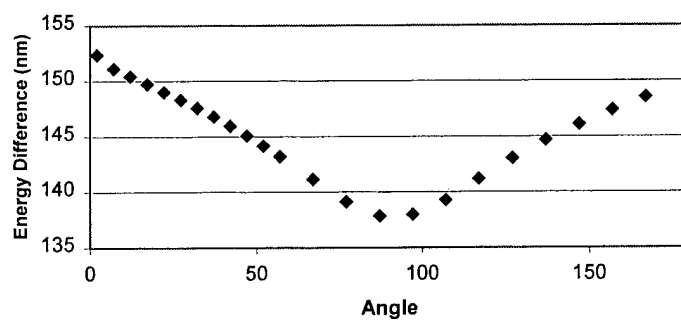


Figure 8 Variation in the band gap energy for BP as a function of torsion angle between phenyl rings. The band gap is taken as the HOMO-LUMO energy difference.

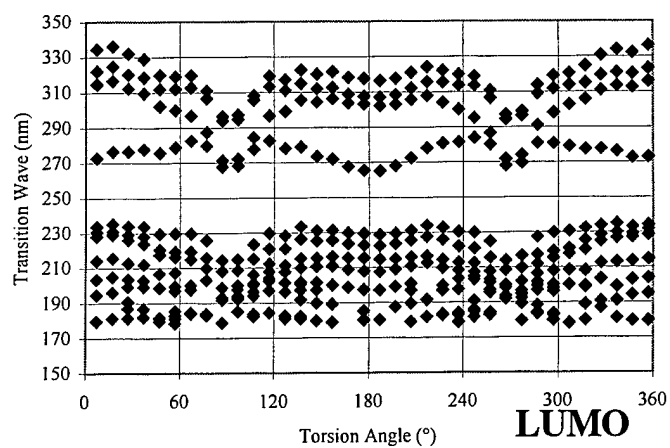


Figure 9 Electronic transition energies for BP as a function of the torsion angle between phenyl rings. Energies above 6.5 eV or with oscillator strengths below 0.05 are omitted.

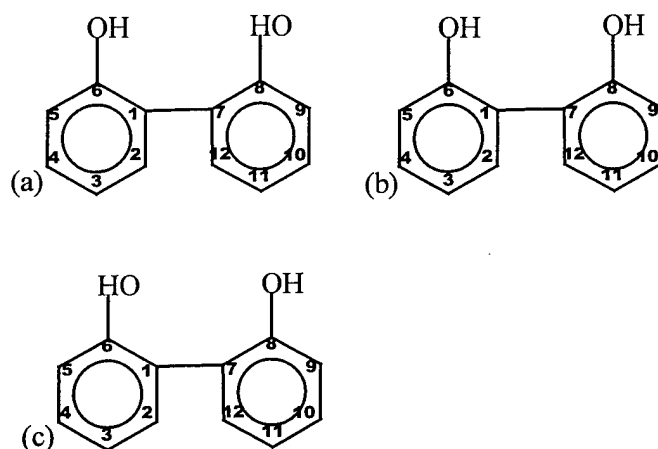


Figure 10 Schematic illustration of the three hydroxyl group orientations found in BP. (a) cis, (b) head-to-tail, and (c) trans.

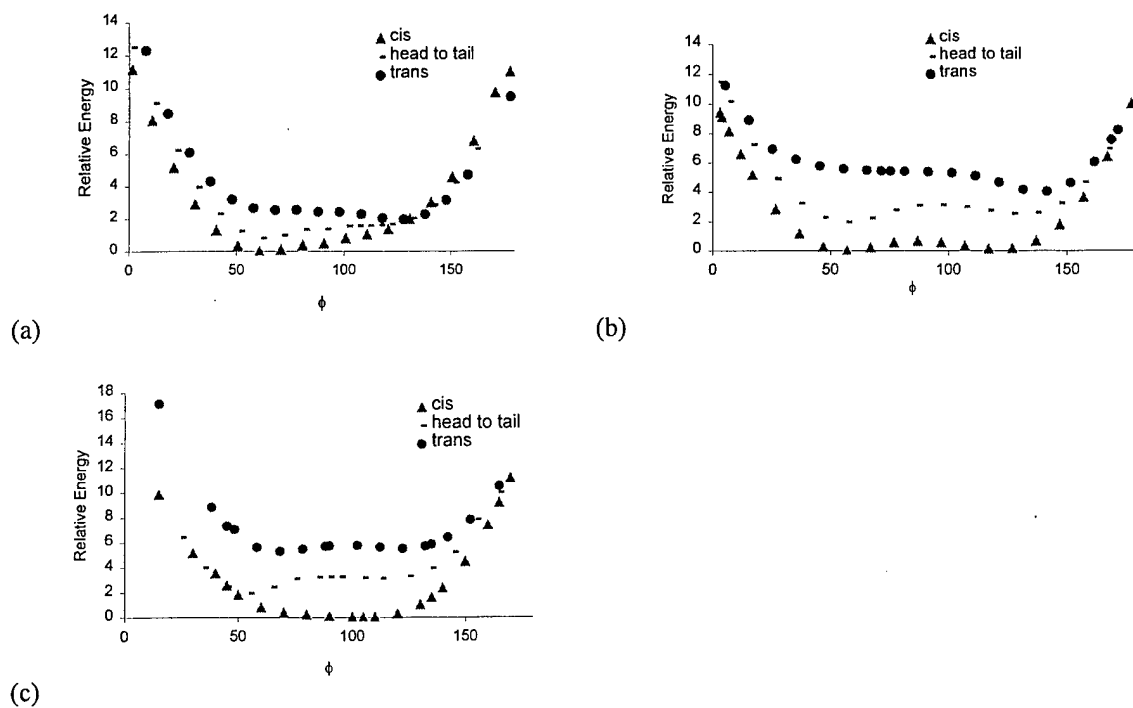


Figure 11 Torsion potential curves for the three conformations of BP relative to their hydroxyl group orientation (a) ab initio 6-31G*, (b) semi-empirical AM1, and (c) MM3 force field with π bonding corrections.

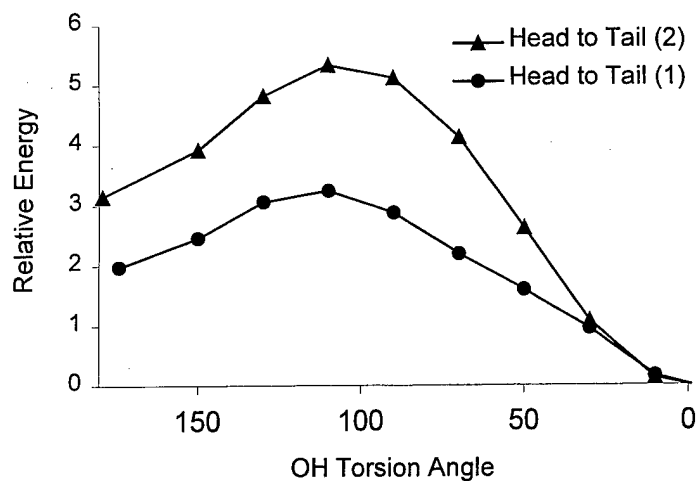


Figure 12 Energy variation (kcal/mol) in changing from head-to-tail to cis BP conformation as determined by ab initio 6-31G* calculations. Curve (1) uses the geometry of the global minimum from the 6-31G* head-to-tail potential curve as the starting point. Curve (2) uses the geometry of the local minimum at 113° in the 6-31G* head-to-tail potential energy curve as the starting point. The more planar OH group is used as the reaction coordinate.

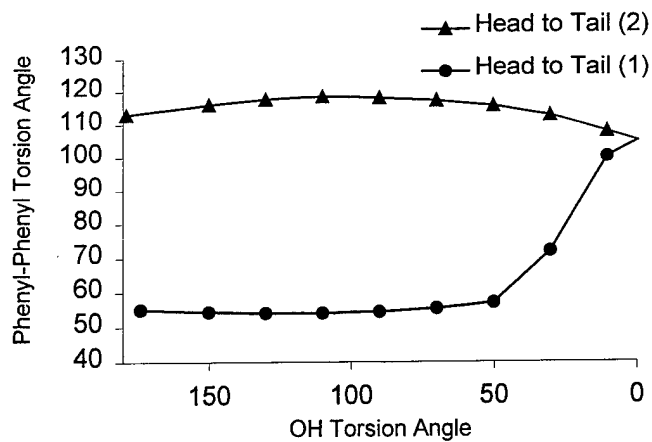


Figure 13 Interdependence of OH group and phenyl torsion angles. Curve (1) uses the geometry of the global minimum from the 6-31G* head-to-tail potential curve as the starting point. Curve (2) uses the geometry of the local minimum at 113° in the 6-31G* head-to-tail potential energy curve as the starting point. The more planar OH group is used as the reaction coordinate.

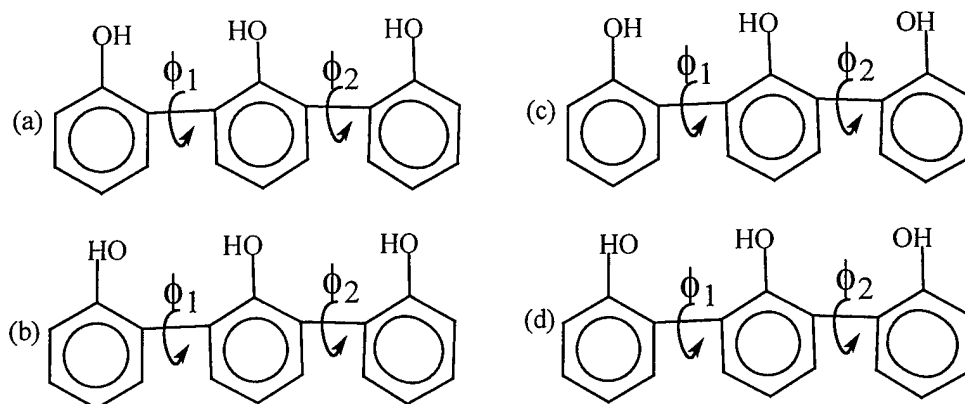


Figure 14 Four potential conformations of triphenol differentiated by the orientations of the hydroxyl groups (a) cis, head-to-tail, (b) head-to-tail, head-to-tail, (c) cis, trans, and (d) head-to-tail, trans.

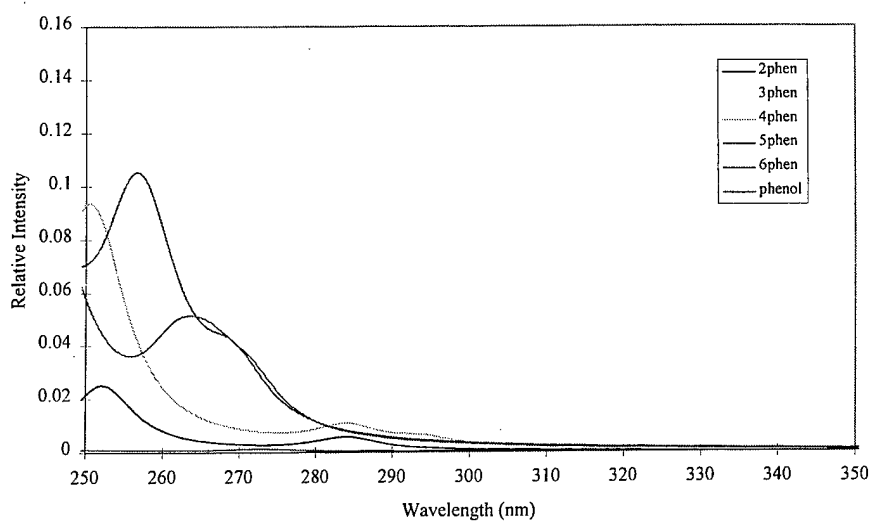


Figure 15 Simulated electronic absorbance spectra for neutral phenolic oligomers.

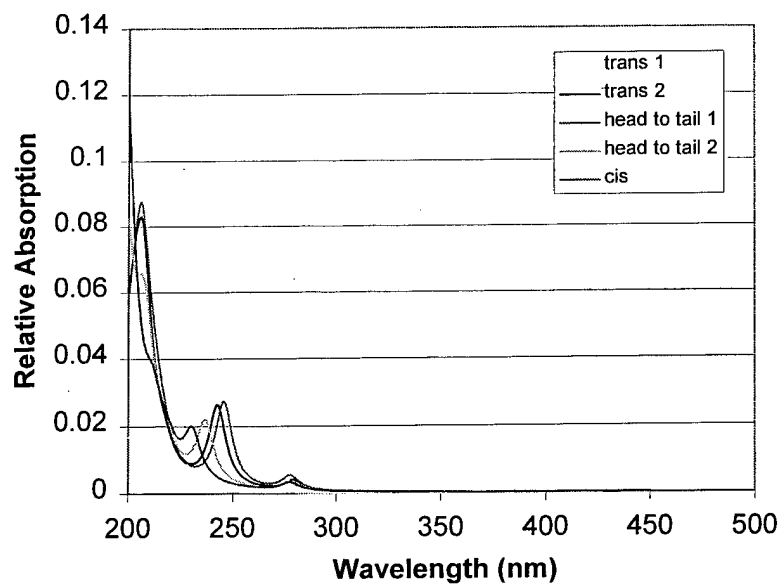


Figure 16 Simulated electronic absorption spectra for five different energy conformations of BP.

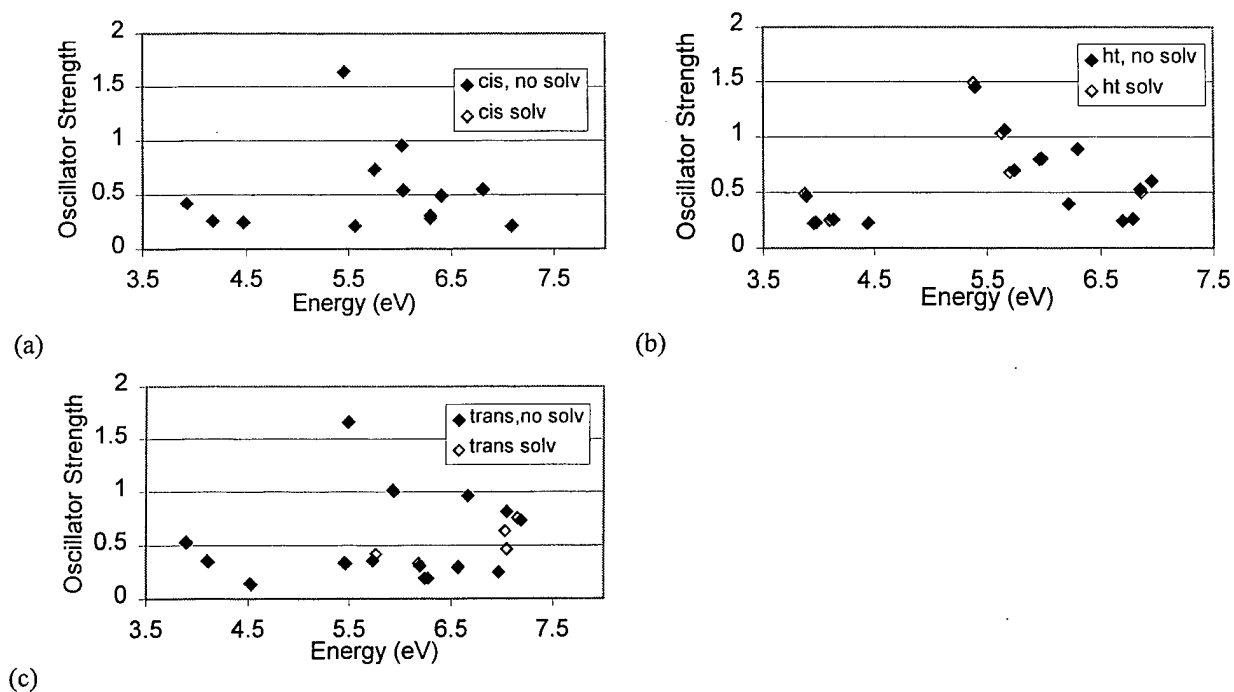


Figure 17 Comparison of the gas phase and solution ($\epsilon=78.3$) electronic absorption energies for the three conformations of BP (a) cis, (b) head-to-tail, and (c) trans.

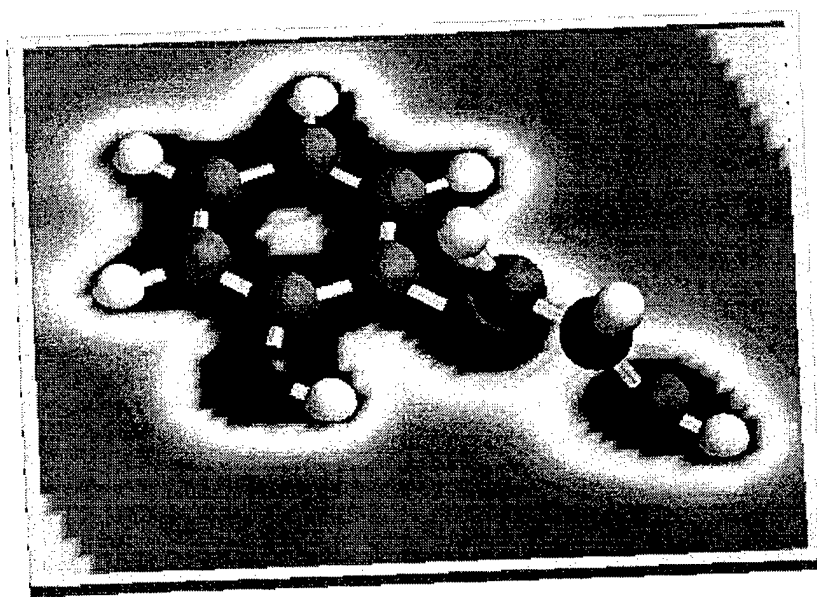


Figure 18 Electron density slice for the cis form of BP. The electron density plane is oriented on the plane of a phenyl ring including the hydroxyl group, bisecting the adjacent phenyl moiety.

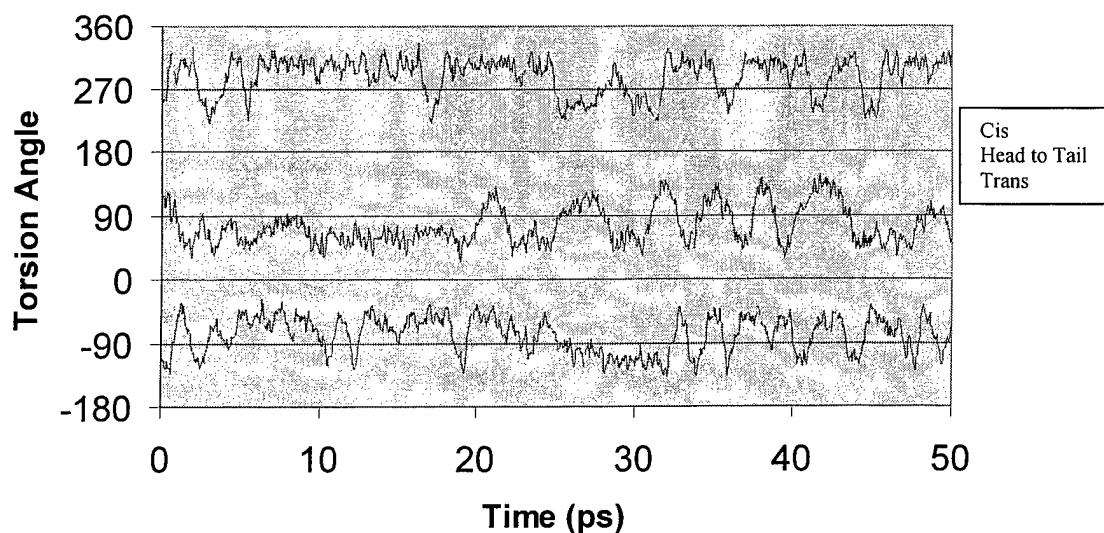


Figure 19 Time evolution of the torsion angles between rings of a four phenol oligomer as sampled from a 50ps molecular dynamics simulation using the recalibrated MM3 force field.

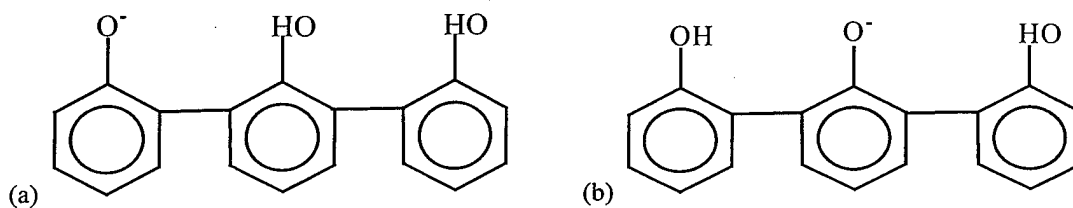


Figure 20 Two examples of the anionic phenol oligomers studied (a) single-sided phenolate oligomer with three rings (two phenol rings neighboring the phenolate on the same side) (b) double-sided phenolate oligomer with three rings (one neighboring phenol ring on either side of the phenolate).

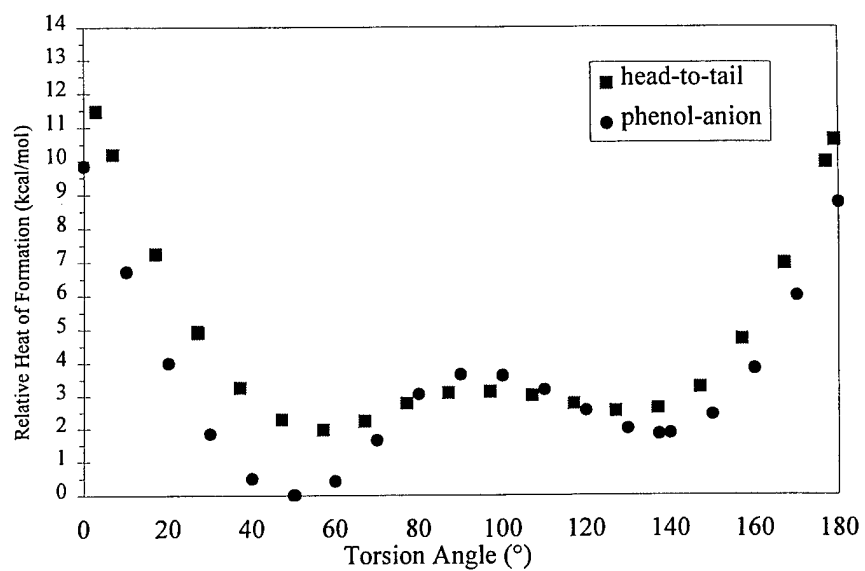


Figure 21 Comparison of the torsional potential for neutral head-to-tail phenol and the phenolate anion.

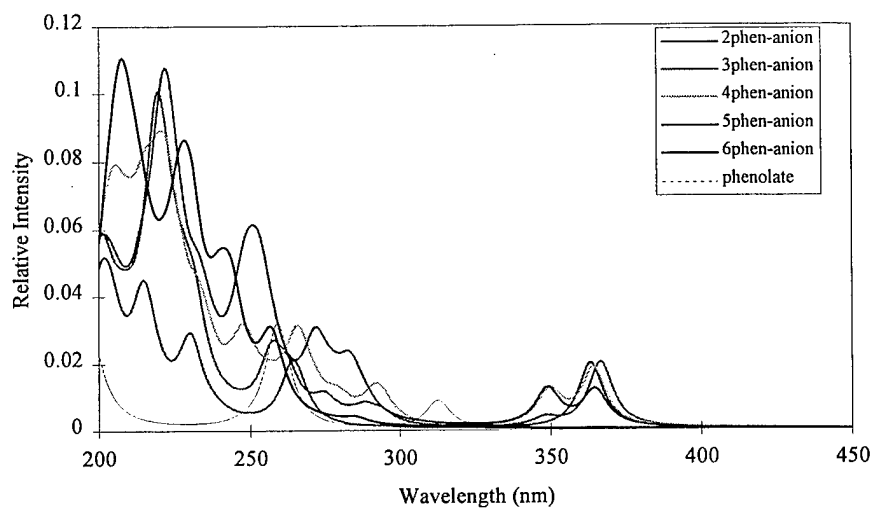


Figure 22 Simulated electronic absorption spectra for anionic phenolic oligomers.

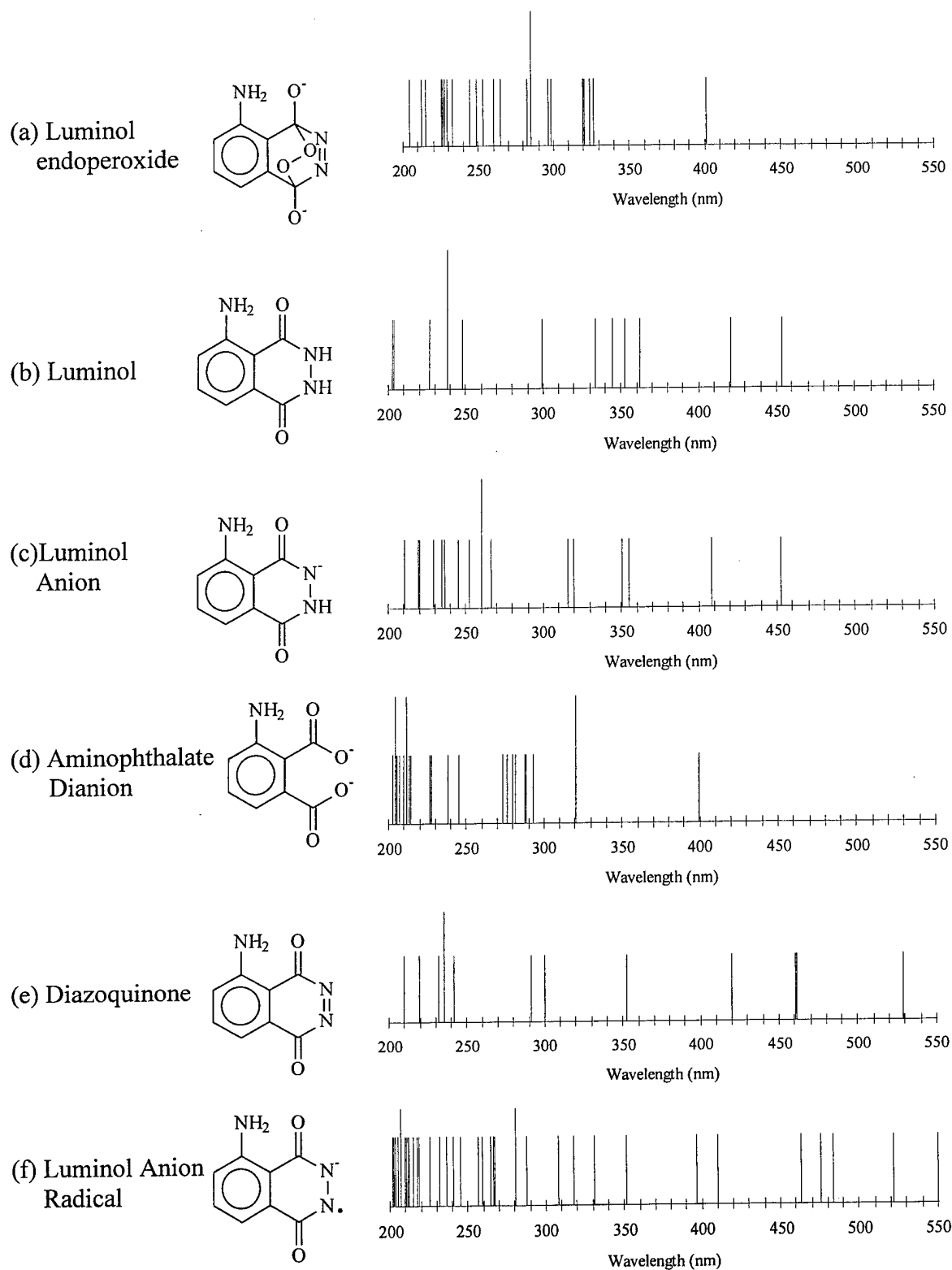


Figure 23 Predicted triplet transition energies ($\lambda < 550$ nm) for proposed electroluminescent forms of luminol. Proposed structures taken from ref. Xx.

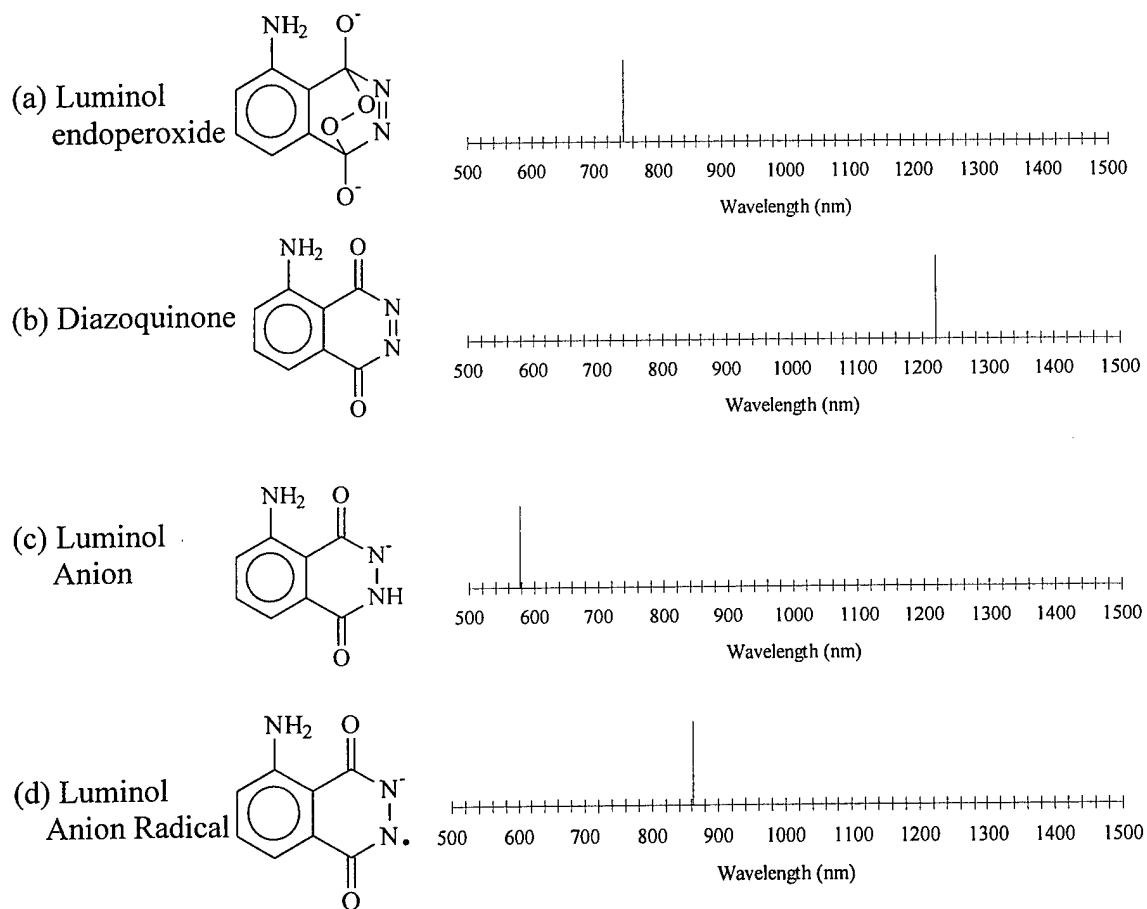
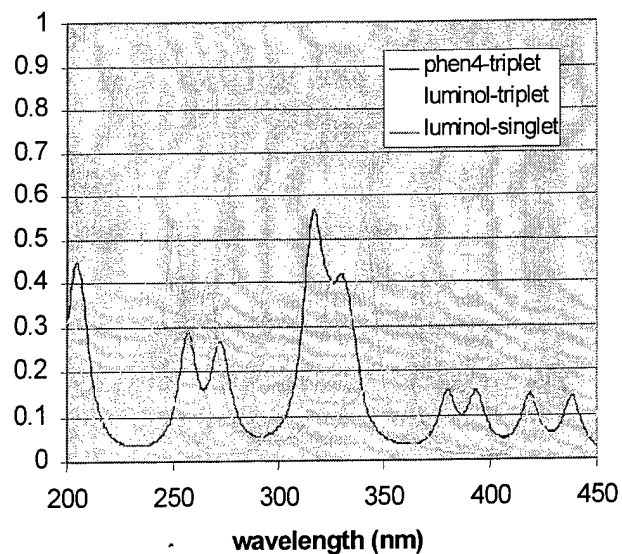
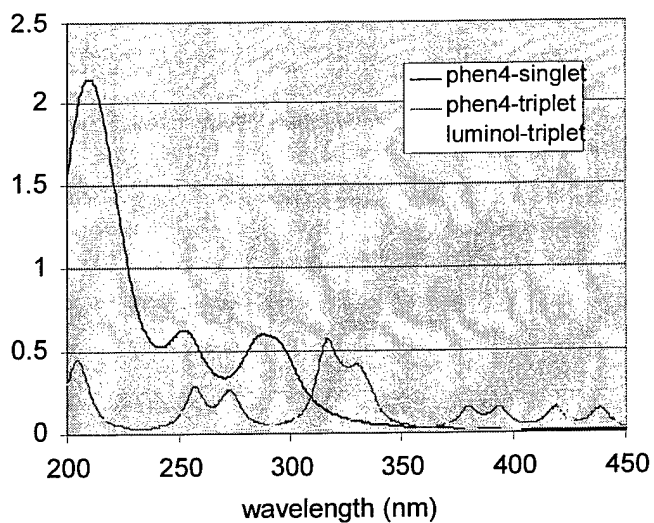


Figure 24 Predicted triplet transition energies ($\lambda > 550$ nm) for proposed electroluminescent forms of luminol. Proposed structures taken from ref. Xx.



(a)



(b)

Figure 25 Predicted spectra for a four phenol oligomer and luminol. Triplet intensities (which are much smaller) have been magnified to allow illustration on the same plot (a) the triplet and singlet states for luminol and the triplet spectra for a four phenol oligomer (b) the singlet and triplet states for the four phenol oligomer with the triplet states for luminol.

Appendix A: Reference and Background Database

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